



Anaerobic digestion for global warming control and energy generation—An overview

Tasneem Abbasi, S.M. Tauseef, S.A. Abbasi*

Centre for Pollution Control and Environmental Engineering, Pondicherry University, Pondicherry 605014, India

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ABSTRACT

Anaerobic digestion often generates 'biogas' – an approximately 3:1 mixture of methane and carbon dioxide – which has been known to be a 'clean' fuel since the late 19th century. But a great resurgence of interest in biogas capture – hence methane capture – has occurred in recent years due to the rapidly growing spectre of global warming. Anthropogenic causes which directly or indirectly release methane into the atmosphere, are responsible for as much as a third of the overall *additional* global warming that is occurring at present. Hence the dual advantage of methane capture – generating energy while controlling global warming – have come to the fore.

This paper presents an overview of the natural and the anthropogenic sources that contribute methane to the atmosphere. In this context it underscores the urgency with which the world must develop and enforce methods and practices to enhance methane capture.

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* Corresponding author. Tel.: +91 9443265262; fax: +91 4132655263.

E-mail address: prof.s.a.abbasi@gmail.com (S.A. Abbasi).

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1. 'Biogas'

When organic matter – such as food, plant debris, animal manure, sewage sludge, and biodegradable portions of municipal solid waste – undergoes decomposition in absence of free oxygen, it normally generates a gas which consists of 40–70% methane, the rest being mostly carbon dioxide with traces of other gases [1–3]. If ignited, this gas burns cleanly (i.e. gives off no soot or foul smell) similar to LPG (liquefied petroleum gas) or CNG (compressed natural gas). This gas is commonly called 'biogas' which is an inexact and imprecise term because the gas which is produced by aerobic decomposition (carbon dioxide) is also 'biogas' in the sense that it is also a result of biodegradation just as the other biogas is. But the word 'biogas' has come to be used exclusively to denote the combustible CH_4 – CO_2 mixture (besides traces of other gases) that is generated by the anaerobic decomposition of organic matter. Biogas has good calorific value, though lesser than LPG and CNG (Table 1).

It must be mentioned that a mixture of CH_4 and CO_2 is not the only gas possible by anaerobic degradation of organic matter. Of the two, methane is produced only if methanogenic bacteria are involved in the anaerobic decomposition [4]. Under different conditions, and with other species of anaerobic microorganisms, gases such as hydrogen and hydrogen sulfide may be generated instead of methane [5,6]. But methanogenic bacteria occur very commonly in nature and in most instances anaerobic digestion does result in the generation of the predominantly CH_4 – CO_2 mixture which is widely referred as 'biogas'.

1.1. A brief history of biogas

Generation of methane by anaerobic digestion of organic matter has been witnessed since time immemorial and has given rise to the phrase *will-o'-the-wisp* which has been inspired by the sight of a bluish moving light that is sometimes seen at night on soft wet ground [7]. We know now that this light is formed due to ignition of methane released by the anaerobic digestion of organic matter present above or in wet soil. One of the first records of the description of the *will-o'-the-wisp* phenomena are attributed to the Roman

scholar Pliny, who noted it around 50 BC. There is evidence that in the years around 10 BC, biogas was used in Assyria for heating baths but little information is available about later years [8].

In the 17th century, Van Helmont also recorded that decaying organic material produced flammable gases. In 1776, Volta resolved that there was a direct connection between how much organic material was used and how much gas the material produced [9,10]. That this combustible gas is methane was established by the work conducted independently by John Dalton and Humphrey Davy during 1804–1808 [11].

Bechamp in 1868 and Popoff in 1875 reported that the formation of methane during the decomposition of organic matter was through a microbiological process [12,13]. Omelianski, in the 1890s, isolated microbes responsible for the release of hydrogen, acetic acid and butyric acid during methane fermentation of cellulose [14]. He also reported that methane perhaps formed due to microorganism-mediated reaction between hydrogen and carbon dioxide [15]. Later, in 1910, Sohngen seconded Omelianski's findings [14]. He also reported that fermentation of complex materials occurs through oxidation–reduction reactions to form hydrogen, carbon dioxide and acetic acid. He demonstrated that hydrogen then reacts with carbon dioxide to form methane. He also assumed that acetic acid through decarboxylation forms methane. This assumption remained highly controversial for decades but is now known to be essentially correct [15].

In 1984 Louis Pasteur produced 100 L of biogas from the fermentation of horse dung collected from Paris roads. He claimed that this production rate should be sufficient to cover the energy requirements for the street lighting for Paris. Parisians did not follow up on it but by 1987 the street lamps of Exeter, in Britain, were running on biogas which was produced from wastewater rather than horse dung. These developments suggested that more and more biogas could be produced by anaerobic digestion of a variety of wastes [8].

In Germany methane gas was first sold to the public gas works in the year 1923. In the following years the practice became more and more common in Europe. The popularity of biogas steadily rose up till the 1950s when increasing availability and falling prices of fossil fuel made biogas energy less and less attractive, especially in developed countries [8]. In developing countries, however, the use

Table 1
Comparison of the calorific values of various fuels [165,166].

Fuel	Calorific value (CV) (approximate)	Indirect emission factor ($\text{kgCO}_2\text{e/GJ}$, net CV basis)
Petrol	10 800 kcal per kg	12.51
Natural gas	8600 kcal per m^3	5.55 ^a
Liquefied natural gas	13 140 kcal per kg	20.00
Liquefied petroleum gas	10 800 kcal per kg	8.00
Kerosene	10 300 kcal per kg	13.34
Diesel	10 700 kcal per kg	14.13
CNG	8600 kcal per m^3	8.36
Biogas	5000 kcal per m^3	0.246 ^b

^a Natural gas European Union mix.

^b Direct CO_2 emissions (emission factor, $\text{gCO}_2\text{e/kWh}$).

Table 2
Top five methane-emitting countries: 2005 [167].

Country	Kt of CO ₂ equivalent ^a	% of world total ^a
China	1,333,098.1	18.7
India	583,977.6	8.2
United States of America	548,073.7	7.7
European Union	535,846.8	7.5
Brazil	492,160.7	6.9

^a These methane emissions are those stemming from human activities such as agriculture and from industrial methane production.

of biogas as a source of energy has remained popular, and has been patronized by the governments. China and India in particular, have increasingly expanding biogas programmes [16].

2. Biogas and global warming

An entirely new dimension to the implications of anaerobic digestion has been added in recent years. This has occurred after the impacts of global warming have become apparent and after the world has arrived at an almost complete consensus that global warming is neither a figment of some people's imagination, nor an hyped-up possibility (as a lot of people believed till a few years back), but a very real and a very serious threat to the entire world [9,16–23].

It is also now a well-accepted fact that methane is a powerful greenhouse gas, each molecule of methane causes about 25 times more global warming than a molecule of CO₂ [24]. If we do not process organic waste and recover methane from it but, instead, allow the waste to rot in the open we will let the methane escape into atmosphere to cause global warming [17]. The dung or rumen lying in the open, the biodegradable part of municipal solid waste which is dumped here and there; the dead plants decaying at the bottom of lakes and ponds; the human excreta or sewage disposed on land, the wastewaters high in COD of food processing, tanneries, distilleries and other industries discharged in public swears, etc.,—all of these emit methane [25–28]. Consequently they all contribute to global warming. Methane is anyway generated in nature as a result of the decay of plant and animal matter but there are also natural sinks which remove excess methane [29,30]. Due to this natural balance between the sources and the sinks of methane, the tropospheric methane levels have hovered around 700 parts per billion for thousands of years [31–35]. But the extra methane generated due to anthropogenic activities over the last 200 years has contributed to the rise of tropospheric methane levels by 150% [36]. As each molecule of methane has global warming (GW) potential 25 times greater than the GW potential of a molecule of CO₂, the 'radiative forcing' by methane along with other non-CO₂ 'Kyoto gases' (nitrous oxide, hydrofluorocarbons, perfluorocarbons and SF₆) constitute roughly one-third of total CO₂ equivalent emissions based on 100-yr global warming potentials [37]. The IEA (2012) statistics reveal that for the year 2005 (Table 2) China leads the world in methane emissions, followed by India and the USA. The contribution of different sources of methane to global warming, in comparison to sources of CO₂ and N₂O, is represented in Fig. 1.

3. Sources of methane

Methane is emitted, either as a component of 'biogas' or as stand-alone emission, from a variety of both anthropogenic (human-related) and natural sources [38–40]. Anthropogenic activities include fossil fuel production, animal husbandry (enteric fermentation in livestock and handling of manure), agriculture (especially rice cultivation), biomass burning, and treatment/disposal systems for biodegradable liquid/solid wastes [39,41,42]. Tables 3 and 4 show the global estimate of methane

Table 3
Global estimates of natural methane sources [28].

Natural sources	Average methane flux (Tg CH ₄ /yr)	Range
Wetlands	174	100–231
Lakes	30	10–50
Termites	22	20–29
Oceans, estuaries and rivers	9.1	2.3–15.6
Geological	9	4–14
Wild animals	8	2–15
Hydrates	5	4–5
Wild fires	3	2–5
Permafrost	0.5	0–1
Total	260.6	157.3–352.6

Table 4
Projections for global anthropogenic methane emissions (based on data from [168]).

Sector	Methane emission (TgCH ₄)		
	2010	2020	2030
<i>Energy</i>			
Fugitives from natural gas and oil systems	75.96	85.19	93.89
Fugitives from coal mining activities	24.54	32.08	37.63
Stationary and mobile combustion	11.65	13.80	16.92
Biomass combustion	9.70	10.24	10.91
Other energy sources	0.02	0.02	0.02
<i>Agriculture</i>			
Enteric fermentation	90.74	100.15	108.98
Rice cultivation	34.87	34.88	35.20
Manure management	11.28	11.87	12.55
Other agricultural sources	20.02	20.02	20.02
<i>Industrial process</i>			
Industrial processes	0.32	0.32	0.32
<i>Waste</i>			
Landfilling of solid waste	38.05	40.72	43.34
Wastewater	21.42	23.54	25.30
Other waste sources	0.73	0.73	0.73
Total	339.30	373.56	405.81

from natural as well as anthropogenic sources. By now a concentration of about 1.8 ppm, on a 'mole fraction in dry air' basis, has been built up in the atmosphere [43]. It presents atmospheric mole fraction of 2.5 times higher than that observed in ice cores dated to AD 1000–1750 and is higher than that observed throughout the existing ice-core record, which spans the past 800,000 years [44,45]. The atmospheric increase of methane since 1750 implies

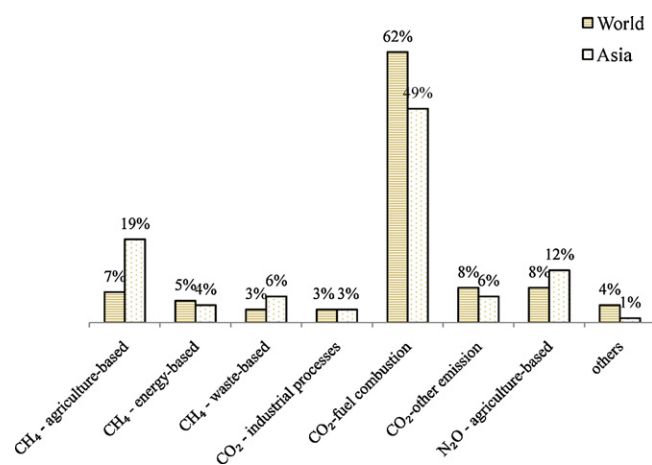


Fig. 1. Relative contributions of different sources of greenhouse gas emissions in the world and in Asia.

Table 5

Global methane emissions from enteric fermentation in 2004 [62].

Region/country	Emissions (million tonnes CH ₄ per year by source)					Total
	Dairy cattle	Other cattle	Buffaloes	Sheep and goats	Pigs	
Sub-Saharan Africa	2.30	7.47	0.00	1.82	0.02	11.61
Asia ^a	0.84	3.83	2.40	0.88	0.07	8.02
India	1.70	3.94	5.25	0.91	0.01	11.82
China	0.49	5.12	1.25	1.51	0.48	8.85
Central and South America	3.36	17.09	0.06	0.58	0.08	21.17
West Asia and North Africa	0.98	1.16	0.24	1.20	0.00	3.58
North America	1.02	3.85	0.00	0.06	0.11	5.05
Western Europe	2.19	2.31	0.01	0.98	0.20	5.70
Oceania and Japan	0.71	1.80	0.00	0.73	0.02	3.26
Eastern Europe and CIS	1.99	2.96	0.02	0.59	0.10	5.66
Other developed	0.11	0.62	0.00	0.18	0.00	0.91
<i>Total</i>	15.69	50.16	9.23	9.44	1.11	85.63
<i>Livestock production system</i>						
Grazing	4.73	21.89	0.00	2.95	0.00	29.58
Mixed	10.96	27.53	9.23	6.50	0.80	55.02
Industrial	0.00	0.73	0.00	0.00	0.30	1.04

^a Excludes China and India.

anthropogenic emissions of $340 \pm 50 \text{ Tg CH}_4 \text{ yr}^{-1}$, or nearly two-thirds of present total emissions, assuming a constant lifetime [45].

It is estimated that more than 60% of global methane emissions are related to these anthropogenic activities [24].

Methane is also released in nature from wetlands, gas hydrates, permafrost, termites and other rumens, oceans, freshwater bodies, non-wetland soils, and other sources such as degrading vegetation and wildfires [46].

The extent of methane emission from a source can vary significantly from one country or region to another; depending on factors such as climate; manner of industrial, agricultural and waste management practices; and extent of provision available for methane capture [47]. Temperature and moisture have a particularly significant effect on the anaerobic digestion process, which is one of the key biological processes that cause methane emissions in both human-related and natural sources [16,47]. Also, the implementation of technologies to capture and utilize methane from sources such as landfills, coal mines, and manure management systems affects the emission levels from these sources [47].

4. Human-related sources

4.1. Landfills

Methane is generated in landfills and open dumps as biodegradable component of the waste contained in them decomposes under anaerobic conditions (i.e. in absence of free oxygen) [48]. The amount of methane evolved depends on the quantity and moisture content of the waste and the design and management practices at the site [49]. Landfills are among the largest human-related sources of methane in developed countries [50]. In some of the developed countries, for example the USA, landfill also happens to be the biggest anthropogenic source of methane, accounting for 34% of all methane emissions [50].

4.2. Natural gas and petroleum systems

Natural gas is largely made up of methane. Hence methane losses occur during the production, processing, storage, transmission, and distribution of natural gas [51]. Because gas is often found in conjunction with oil; the production; refinement, transportation, and storage of crude oil also leads to similar fugitive methane emissions [52,53].

4.3. Coal mining

Methane lies trapped in coal deposits and in the surrounding strata. Mining operations, in both underground and surface mines, 'unlock' this methane, leading to its release [54,55]. In addition, handling of the coal after mining results in methane emissions [39].

4.4. Livestock enteric fermentation

Among domesticated livestock, ruminant animals (cattle, buffalo, sheep, goat, and camel) produce significant amounts of methane as part of their normal digestive processes [56–58]. In the rumen (large fore-stomach) of these animals, microbial fermentation converts feed into products that can be digested and utilized by the animal [59–61]. This microbial fermentation process (enteric fermentation) produces methane as a by-product, which is exhaled by the animal. Methane is also produced in smaller quantities by the digestive processes of other animals, including humans, but emissions from these sources are insignificant [47]. It was estimated in 2004 that about a million tonnes of methane was being emitted by livestock ([62]; Table 5). Considering that, as per the Food and Agricultural Organization (FAO) the production of livestock has continued to increase 'dramatically' [62], this figure is expected to have crossed 90 million tonnes by now.

4.5. Handling manure management

Livestock manure keeps releasing methane due to the anaerobic decomposition of organic material contained in the manure by bacteria exited along with the manure by the animal [63–65]. Manure deposited on fields and pastures, or otherwise handled in a dry form, produces significant amounts of methane. Manure lagoons and holding tanks, which are commonly used at larger dairy and swine operations, also release significant quantities of methane [62,66].

4.6. Wastewater treatment

In the course of treatment of biodegradable wastewater from domestic and industrial sources for removing soluble organic matter, suspended solids, pathogenic organisms, and chemical contaminants, methane is produced and is released to atmosphere whenever anaerobic conditions develop [67–70]. This may happen often with the sludge that separates during sedimentation due to

Table 6

A summary of reports on methane emissions from paddy fields in India, indicating wide variations between site to site.

State/region	Specific site	Period and frequency of observations	Methane emissions (mg/m ² h)	Reference
New Delhi	National Physical Laboratory	0, 15, and 30 min	0.06–0.62	[169]
New Delhi	National Physical Laboratory	Every 15 min for 30 min	41.73	[170]
Orissa	Not stated	June to November, 1994; 3 h intervals over a 24 h period	-	[171]
Uttar Pradesh	Institute of Agricultural Sciences, Banaras Hindu University	At 4 h intervals during one day of each month.	2.14–8.23	[172]
New Delhi	Indian Agricultural Research Institute, New Delhi	July–November 2004; Interval of 15 min for 1 h	8040–20,920 (IARI Soil)	[172]
Orissa	Central Rice Research Institute, Cuttack	June–October 1994; 9.00–9.30 h and 15.00–15.30	1047–10910 (Raipur soil)	[173]
Orissa	Not stated	June to November, 1994; 9.00–9.30, 15.00–15.30	13.16	[174]
Orissa	Central rice research institute	January–May 1997	192.08–843.75	[175]
New Delhi	Indian Agricultural Research Institute, New Delhi	9.00–9.30, 15.00–15.30	8.15	[176]
Orissa	Research farm of Central Rice Research Institute, Cuttack	July–October	15.6–27.2	[177]
Orissa	Central rice research institute, Cuttack	1995–1998	4.13–16.36	[177]
New Delhi	Indian Agricultural Research Institute, New Delhi	January–May, July–December; 09.00–09.30 and 15.00–15.30 h	0.125	[178]
Delhi	Indian Agricultural Research Institute (IARI)	January–May, July–December 1997	9.00–9.30, 15.00–15.30	[178]
New Delhi	Indian Agricultural Research Institute, New Delhi	4 years	0.59	[179]
Assam	Kahikuchi, Guwahati	Every 10 min for 20 min	2557–1833	[179]
Orissa	Central Rice Research Institute (CRRI), Cuttack	July–October 1994–1997	2450–3720	[180]
Orissa	Balianta	Every 0, 10, and 20 min	9740–11310	[181]
Assam	–	105 days; every 20 min for 40 min	30858–40877	[182]
Gujarat	Lambhavel, Central Gujarat	4 months; Every 15 min for 45 min	0.29–1.36	[183]
Orissa	Central Rice Research Institute, Cuttack	January–May, June–December, 2000	8830–18630	[184]
Orissa	Central Rice Research Institute (CRRI), Cuttack	June to November, November to February; 0, 5, 15, 30 min interval.	Site I – 105.67–720.64 Site II – 201.59–430.94	[185]
Punjab	Punjab Agricultural University, Ludhiana	February–April every 15 days	17.59	[185]
Lucknow	Lucknow	9.00–5.00 for every 2 h	1.17–2.52	[186]
Uttar Pradesh	Environmental field station of the National Botanical Research Institute, Lucknow.	Every 15 min for 60 min, twice a day	0.04 and 0.93	[187]
Orissa	Central Rice Research Institute, Cuttack	June to December, 2005; 9.00–9.30, 15.00–15.30	315.1–204.7	[187]
Punjab	Punjab Agricultural University, Ludhiana	2005–2006	8.529–14.44	[188]
India	–	11 am–12 noon	0.18–0.35	[189]
		At 11, 16, 25, 38, 56, 83, 94 and 108 days Every 0, 15 and 30 min	2.20–0.56	[77]
		–	1.5–0.6 CO ₂ eq	[189]

the high BOD of the sludge; this rapidly leads to the total depletion of dissolved oxygen in the sludge and development of anaerobic conditions, resulting in methane emissions [46,71,72]. These emissions can be avoided by treating the wastewater and the associated sludge under aerobic conditions or by capturing methane that is released under anaerobic conditions [47,73].

4.7. Agriculture

Methane is produced during agriculture whenever anaerobic conditions develop. This happens most significantly in the paddy fields flooded for rice cultivation [24,74,75]. Flooded soils are ideal environments for methane production because of their high levels of organic substrates, oxygen-depleted conditions, and moisture [76,77]. The level of emissions varies with soil conditions, type of cultivar, agricultural practices, and climate. Tables 6 and 7, which

summarize data pertaining to rice paddies of India, provide an indication of the very wide variation in methane emissions that is possible between one paddy field and the other. By suitably modifying the agricultural practices, methane emissions from rice cultivation can be significantly reduced [78,79].

5. Opportunities of methane capture

Whereas coal mining, and production of natural gas/oil generates nearly pure methane, the other five anthropogenic activities listed in the preceding section produce the methane–CO₂ mixture that is usually called 'biogas'. Of these five activities, the quantities of biogas exhaled by livestock are difficult to control and there is little that can be done about it. Of the remaining four activities, agriculture can be made a lesser emitter of methane by proper soil and water management, and proper choice of cultivar,

Table 7Seasonal integrated flux (E_{sif}) of methane as estimated at various sites; this again reflects very high inter-site variation.

State/region	Specific site	Period and frequency of observations	Methane emissions $E_{\text{sif}} = \text{mg/m}^2$	Reference
Uttar Pradesh	Banaras Hindu University, Varanasi	Not stated	20,775	[190]
Orissa	CRRF Farms, Cuttack	1 year	30,175	[191]
Orissa	Chilka, Gahirmatha, Anshupa	1997–2000; March to June, July to October, November to February; 0, 15, and 30 min	0.83–4.71	[192]
Assam	Amalopam, Tezpur University	2 years sampling was done for once in 7 days, twice a day (at 9 am and 2 pm) and regular interval of 15 min for an hour	6435	[193]
Assam	Amalopam, Tezpur University	do	1170	[193]
Assam	Amalopam, Tezpur University	do	10,600	[193]
Assam	Kahikuchi, under lower Brahmaputra valley zone	Once in a week every 0, 15, 30, 45 min	Pre-monsoon 7510 Monsoon 16,390	[194]
Assam	II Sites Amalopam, Tezpur University	April–July, 2006 at 7-day intervals twice a day (at 9 am and 2.00 pm) at a intervals of (0, 15, 30 and 45 min)	Site I 1380 Site II 960	[194]
Andhra Pradesh	NRSA, Hyderabad	Not stated	5020	[195]
Delhi	National Physical Laboratory	1 year	1080	[195]
Kerala	RRL, Trivandrum	Not stated	3027	[195]
Orissa	Balianta, near Bhubasnewar	Not stated	5090	[195]
West Bengal	IRPE, Gabberia	Not stated	18,010	[195]
Assam	Lakshmikantapur			
Assam	Titabar Farms-AAU, Jorhat (Upper Brahmaputra Valley)	1 year	8160	[195]
Assam	Tezpur	6 months sampling was done for once in 7days, twice a day (9 am and 2 pm) and regular interval of 15 min for an 45 min	10,565	[196]
Assam	North Bank Plain	9.00–14.00 h	8130–13,000	[196]
	Agroclimatic Zone, Tezpur	every 0, 15, 30, 45 min		
India	–	2003 to 2004; 2006 to 2007	34.38 \pm 23.26	[197]

to minimize development of conditions favorable for anaerobic digestion [80–82]. It is the remaining three activities – landfills, handling of manure, and wastewater treatment – which provide opportunities to not only reduce fugitive biogas emissions but also capture much of the generated biogas for use as energy source.

Well-established technology exists for generating biogas from animal manure [83–86]. Likewise several types of reactors are available to anaerobically digest different types of biodegradable wastewaters to obtain biogas [87–90]. By using these technologies, and by careful management of manure and wastewater to reduce fugitive biogas emissions, a major portion of methane generated in the biogas can be captured. A reasonable assumption for the gas collection efficiency for a properly planned gas collection system is 70–85% [91,92]. Municipal solid waste (MSW), phytomass, and other forms of biodegradable solid waste have enormous potential of supplying biogas but there are technological problems yet to be overcome [17,20].

6. Steps associated with the generation of biogas

Anaerobic digestion involves bacterial fermentation of organic wastes in the absence of free oxygen. The fermentation leads to the breakdown of complex biodegradable organics in a four stage process [93,94] (Fig. 2):

1. Large protein macromolecules, fats, and carbohydrate polymers (such as cellulose and starch) are cracked into water soluble monomers (amino acids, long-chain fatty acids, and sugars). This is brought about by exoenzymes (hydrolase) present in facultative and obligatory anaerobic bacteria.

2. These products are then fermented during acidogenesis to form short-chain (C1–C5) 'volatile fatty acids', principally lactic, propionic, butyric, and valeric acid.
3. In acetogenesis, homoacetogenic microorganisms consume these fermentation products and generate acetic acid, carbon dioxide, and hydrogen.
4. Methanogenic organisms, which are strictly anaerobic, consume the acetate, hydrogen, and some of the carbon dioxide to produce methane. Three biochemical pathways are used by methanogens to achieve this [95]: (a) acetotrophic pathway ($4\text{CH}_3\text{COOH} \rightarrow 4\text{CO}_2 + 4\text{CH}_4$); (b) hydrogenotrophic pathway ($\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$); (c) methylotrophic pathway ($4\text{CH}_3\text{OH} + 6\text{H}_2 \rightarrow 3\text{CH}_4 + 2\text{H}_2\text{O}$).

Methylated substrates other than methanol can also be converted. Acetotrophic pathway is the primary one, hence theoretical yield calculations are often made using this pathway [96].

Theoretically, methane formation follows an exponential equation:

$$V_B = C_1(1 - e^{-C_2 t_B})$$

where V_B is the biogas yield ($\text{m}^3 \text{d}^{-1}$), t_B is residence time in the bioreactor (d), and C_1 and C_2 are constants.

Biogas, in theory, should contain equal volumes (50–50) of methane and carbon dioxide. However, acetogenesis typically produces some hydrogen, and for every four moles of hydrogen consumed by hydrogenotrophic methanogens a mole of carbon dioxide is converted to methane [97]. Fats and proteins can yield larger amounts of hydrogen leading to higher typical methane content for these substrates. In certain conditions, these molecules can also get converted to products other than methane. Therefore, the overall biogas yield and methane content varies for different

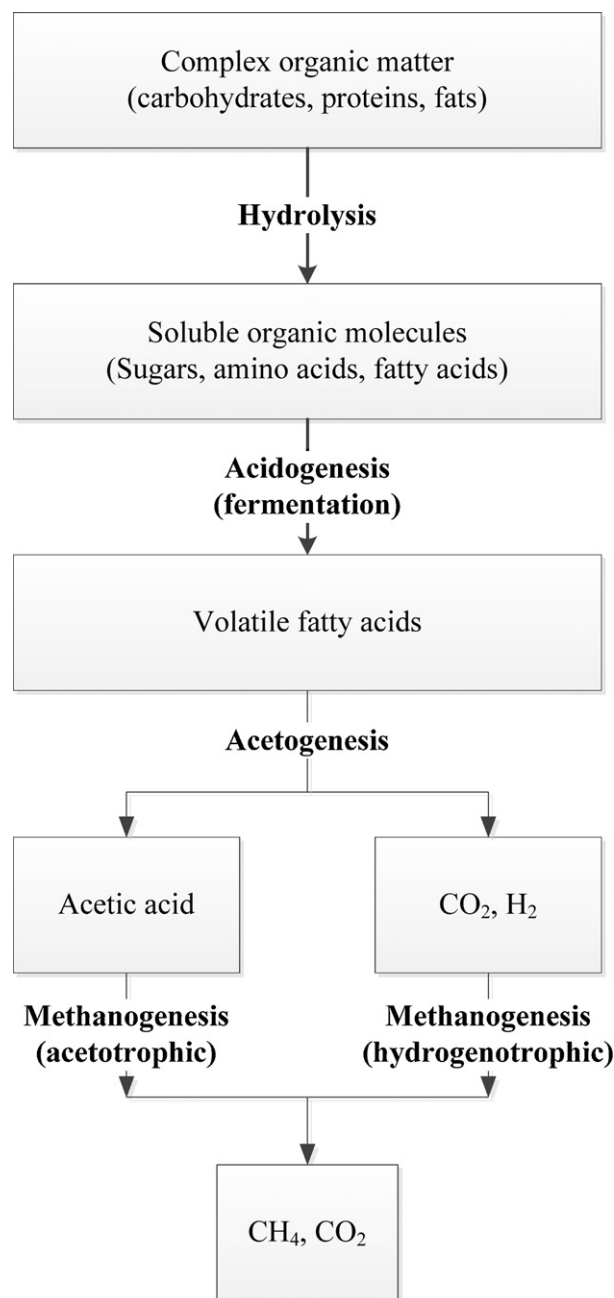


Fig. 2. The steps involved in anaerobic digestion.

Adopted from [97].

substrates, biological consortia and digester conditions [97]. The methane content of biogas can range from 40 to 70% (by volume) but more often than not it is in 55–65% range [98–108].

Wherever biogas is generated – be it from organic matter decomposing under anaerobic conditions in the open, or in captive anaerobic digesters, or in the guts of large ruminant animals, or by termites and some other smaller organisms – these four steps are principally involved. If the process is properly controlled in reactors so that it proceeds optimally as per these stages, the principal end product, the biogas, contains 40–70% (by volume) of methane gas, the rest being carbon dioxide and traces of ammonia, hydrogen sulfide and hydrogen [8]. This 'biogas', which is a convenient and clean fuel, can either be used directly with or without the removal of carbon dioxide or can be converted into electricity with the help

of suitable generators [109,110]. A wide variety of substrates can be used to generate biogas (Fig. 3).

7. Factors which influence anaerobic digestion of an organic substrate

Presence of adequate quantities of nitrogen, micronutrients, and water is essential if an organic substrate is to undergo anaerobic digestion and generate methane-rich biogas [111,112]. These are essentially the requirements of microorganisms named in Table 8, especially methanogenic bacteria. Because these microorganisms are the 'workers' who take the fermentation along the desired route and at optimum pace, generating conditions which help these microorganisms ensures success of the process [16,113].

Some of the aspects which have to be kept in view for successful operation of an anaerobic digestion process for obtaining biogas are recounted below.

7.1. Specific surface of the substrate

Greater the specific surface of the substrate, more efficiently the microorganism–substrate contact; consequently faster the digestion. If the substrate is in the form of large pieces of solids it should be comminuted.

7.2. C/N ratio

The relative proportions of carbon and nitrogen present in an organic material is expressed in terms of the carbon/nitrogen (C/N) ratio. C/N ratio in the range of 16:1–25:1 is considered to be optimum for anaerobic digestion [114–117].

If the C/N ratio is too high, the nitrogen is consumed rapidly by the methanogens to meet their protein requirement and is no longer available to react on the left-over carbon content in the material. As a result the biogas production gets depressed [118].

If the C/N ratio is too low, nitrogen is liberated and accumulates in the form of ammonia. This increases the pH of the material. When pH value rises higher than 8.5 it begins to exert a toxic effect on the methanogenic bacteria [22,119].

Animal waste, such as cow dung, which has been the most preferred feed in low-rate biogas systems, has an average C/N ratio of 24 [120]. Plant materials contain a high percentage of carbon and so the C/N ratio is high [102]; for example rice straw and sawdust have C/N ratios of 70 and >200, respectively (Table 9). Human excreta has a C/N ratio of about 8 [121].

To maintain the C/N level of the digester material at optimum levels, materials of high C/N ratio can be mixed with materials of low C/N ratio [122–124].

7.3. Dilution

Water should be added, if necessary, to the raw material to generate a slurry which is neither too thick nor too thin. If a material is diluted too much, the solid particles may settle down in the digester and may not get degraded properly. If the slurry is too thick, it may be difficult to stir and may impede the flow of gas to the upper part of the digester [103,104]. Different systems can handle different levels of slurry density, generally in the range of 10–25% of solids [16].

7.4. pH

Optimum biogas production is achieved when the pH value of the input mixture is between 6.7 and 7.5 [8,125]. During the initial period of digestion, large amounts of organic acids are produced and the pH of the mixture decreases. As digestion continues and

Table 8

Micro-organisms involved in anaerobic digestion.

Stage	Bacteria
Stage I $(C_6H_{10}O_5)_n + nH_2O = n(C_6H_{12}O_6)$	
Stage II $C_6H_{12}O_6 + 2H_2O = 2CH_3COOH + 4H_2 + CO_2$ $C_6H_{12}O_6 + 2H_2 = 2CH_3CH_2COOH + 2H_2O$ $C_6H_{12}O_6 = CH_3CH_2CH_2COOH + 2CO_2 + 2H_2$ $C_6H_{12}O_6 = 2CH_3CHOHCOOH$ $C_6H_{12}O_6 = 2CH_3CH_2OH + 2CO_2$	<i>Bacteriodes, Clostridium, Butyrivibrio, Eubacterium, Bifidobacterium, Lactobacillus</i>
Stage III $CH_3CHOHCOOH + H_2O = CH_3COOH + CO_2 + 2H_2$ $CH_3CH_2OH + H_2O = CH_3COOH + 2H_2$ $CH_3CH_2CH_2COOH + 2H_2O = 2CH_3COOH + 2H_2$ $CH_3CH_2COOH + 2H_2O = CH_3COOH + CO_2 + 3H_2$	<i>Desulfovibrio, Syntrophobacter wolinii, Syntrophomonas</i>
Stage IV $4H_2 + CO_2 = CH_4 + 2H_2O$ $2CH_3CH_2OH + CO_2 = 2CH_3COOH + CH_4$ $2CH_3(CH_2)_2COOH + 2H_2O + CO_2 = 4CH_3COOH + CH_4$ $CH_3COOH = CH_4 + CO_2$	<i>Methanobacterium formicicum, M. bryantii; Methanobrevibacter ruminantium, M. arboriphilus, Methanospirillum hungatei; Methanosarcina barkeri</i>

the concentration of ammonia increases, due to the digestion of nitrogen, the pH value increases. When the methane gas production stabilises, the pH remains between 7.2 and 8.2 [126].

When plant material is fermented in a batch system, the acetogenesis/fermentation stage is rapid, producing organic acids which reduce the pH and inhibit further digestion [127]. In general a drop in pH and a rise in the proportion of CO_2 in the biogas are indicators of a disturbance in the digestion process. In such situations, reduction in pH can usually be controlled with the addition of lime [128].

7.5. Temperature

Different species of methanogenic bacteria function optimally in three different temperature ranges: 50–65 °C, 20–40 °C, and <1.2 °C. The concerned bacteria are called thermophilic, mesophilic, and psychrophilic, respectively [129]. In laboratory tests, methane formation has been shown to occur even at sub-zero temperatures [130] but outside the thermophilic, mesophilic, and psychrophilic ranges of temperature the concerned microbial consortia is not able to work efficiently. Large-scale anaerobic digestion is generally

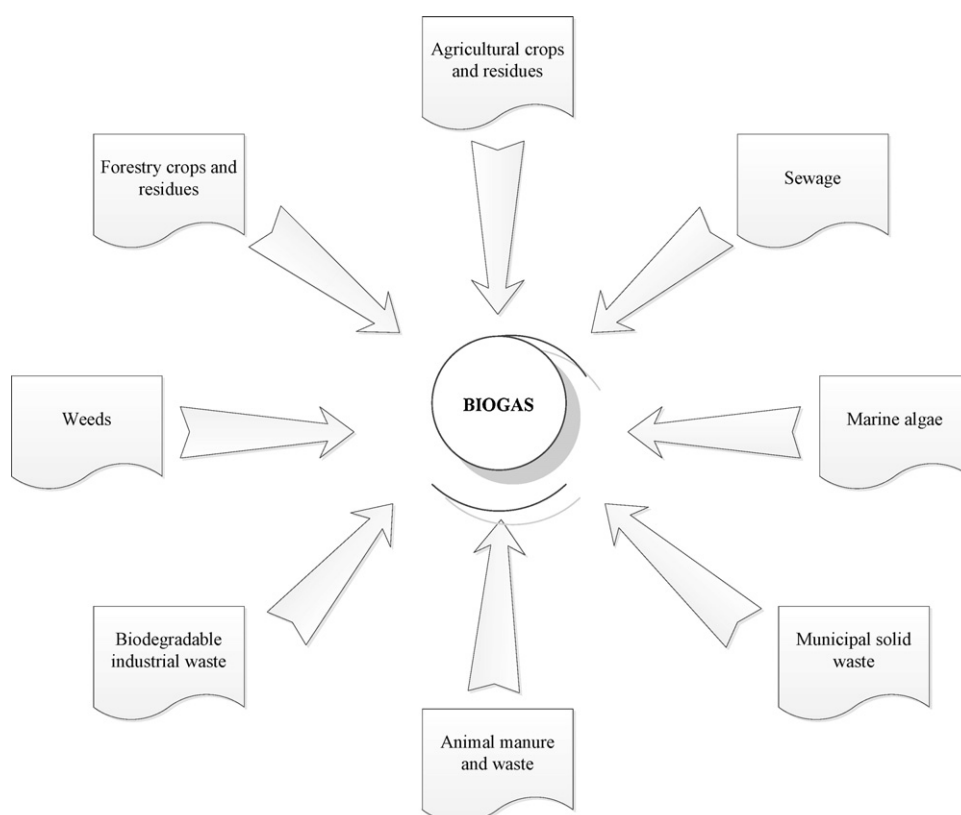
**Fig. 3.** Examples of substrates which can be anaerobically digested to generate biogas.

Table 9
C/N ratio of some biodegradable materials.

Raw material	C/N ratio
Duck dung	8
Human excreta	8
Chicken dung	10
Goat dung	12
Pig dung	18
Sheep dung	19
Cow dung	24
Water hyacinth	25
Municipal solid waste	40
Elephant dung	43
Maize straw	60
Rice straw	70
Wheat straw	90
Saw dust	>200

carried out in the mesophilic mode [100] with lesser number of digesters operating in thermophilic mode and much lesser in the psychrophilic mode [131].

The mesophilic temperature range is between 20 °C and 40 °C but the mesophilic temperature considered to be most suitable for anaerobic digestion is 35 °C [132]. In thermophilic digestion 55 °C is considered to be ideal [132,133].

Although thermophilic anaerobic digestion process is generally more efficient than the mesophilic process, it is more difficult to control and also needs extra energy inputs [134], leading to a less favorable energy balance than mesophilic anaerobic digestion.

7.6. Loading rate

This is an important process control parameter especially when the digestion is carried out in continuous mode – which is how it usually is [135]. Overloading can easily lead to system failure. This can happen if there is inadequate mixing of the waste with slurry. It may cause a significant rise in volatile fatty acids concentration, leading to sharp drop in pH. When this happens feed rate to the system has to be reduced for a while till the process re-stabilizes [16].

7.7. Retention time

'Retention time' is the duration for which organic material (substrate) and microorganisms ('solids') must remain together in a digester to achieve the desired extent of degradation. Shorter the 'substrate retention time' required to achieve this objective in an anaerobic reactor, more efficient the reactor [136]. But to achieve low 'substrate retention times' it is necessary to simultaneously achieve high microorganism ('solids') retention times as explained below.

Hydraulic retention time (HRT): The term commonly used to denote substrate retention time is 'hydraulic retention time'. This is the time which an organic material, sought to be aerobically degraded, spends in a digester from the instant of its entry in to the digester to its exit.

Solids retention time (SRT): 'Solids' is the term commonly used to denote microorganisms in a digester. It is not a precise term because most digester feeds contain suspended solids which are not necessarily made up of live biomass. Hence solids other than microorganisms are also present in an anaerobic digester. Moreover, it is the 'volatile solids' content in any substrate which participates in anaerobic digestion (non-volatile or 'refractory' organics do not). Hence terms such as 'high solids digestion' or 'solid-feed digestion' are also commonly used in the bio-gas field [17,27,106] wherein 'solids' is not meant to denote

microorganisms. So the use of the term 'solid', instead of 'microorganism' in the context of microorganism retention time can be a source of confusion.

Nevertheless it is a part of the established jargon and hence we will also adhere to it. Solids retention time (ST) is the duration for which active microorganisms reside in a digester.

The relationship between HRT and SRT, and the importance of 'food to microorganism ratio': At any given temperature, the microorganisms present in a digester can only consume a limited amount of food each day. Hence in order to digest a given quantity of substrate one must supply adequate number of microorganisms. The ratio of the quantity of substrate and to the quantity of bacteria available to consume that substrate is called the 'food-to-microorganism ratio' (F/M). This ratio is the controlling factor in all biological treatment processes [137,138]. A lower than adequate F/M ratio will result in a greater percentage of the substrate being converted to biogas [139].

The only way in which F/M ratio can be kept adequately low even as we aim to reduce HRT (to enhance digester efficiency), is to find a way by which SRT is kept high. In other words to find ways by which the substrate passes through the digester quickly but microorganisms pass through much more slowly. This situation can ensure that at any given time more quantities of microorganisms are present in a digester than substrate (hence low F/M ratio).

In conventional low-rate digesters and in the continuously stirred tank reactors (CSTRs), there is no provision to retain 'solids' (microorganisms) [16,93]. Hence the solids pass out of the digesters at the same rate as the substrate-to-be-degraded does. In other words in these systems $HRT = SRT$. On the other hand, in high-rate digesters, retention of microorganisms by way of attached growth or suspended growth systems enables $SRT \gg HRT$. In a typical high-rate anaerobic digester, SRT is about three times higher than the HRT [139]. Some attempts have been made to enhance SRT in conventional CSTRs by providing biofilm support systems in them [107].

7.8. Toxicity

Mineral ions, especially of heavy metals, and detergents are among the materials that inhibit the normal growth of bacteria in a digester. Small quantities of minerals (sodium, potassium, calcium, magnesium, ammonium and sulfur) stimulate the bacterial growth, but higher concentrations may be inhibitory [4,125].

Heavy metals such as copper, nickel, chromium, zinc, and lead are essential for bacterial growth in very small quantities, but higher quantities have a toxic effect [140–143]. Detergents such as soap, antibiotics, organic solvents also inhibit the bacteria [4,144]. Recovery of digesters following inhibition by toxic substances can only be achieved by cessation of feeding and flushing the contents or diluting the contents to push the concentration of inhibitory substances to below the toxic level [4,145].

7.9. Mixing/agitation

Mixing is required to maintain fluid homogeneity, hence process stability, within a digester [103,104,146–148]. The objectives of mixing are to combine the incoming material with the bacteria, to stop the formation of scum, and to avoid pronounced temperature gradients within the digester.

Very rapid mixing can disrupt the bacterial community while too slow a stirring can cause inadequate mixing and short-circuiting [149]. The extent of mixing required is also dependent on the content of the digestion mixture [144].

7.10. Pathogens

Certain pathogenic bacteria (e.g., *Salmonella*, *Escherichia coli*, *Listeria*) and viruses present in municipal solid waste can pose risk of infection to the workers handling the waste [150]. Such pathogens are sensitive to temperature, hence most effective pathogen control occurs when anaerobic digestion is performed at thermophilic temperatures and at long retention times. Bendixen [151] found that 90% reduction of a *Salmonella* population was achieved at thermophilic temperature (53 °C) within a mere 0.7 h whereas at mesophilic conditions (35 °C) well over 2 days were necessary [151]. For certain types of wastes, a separate pasteurization step before or after anaerobic digestion at 70 °C for 60 min has been stipulated by the European Union Animal Byproducts Regulation [152]. Pasteurization (70 °C) is an effective alternative to sterilization (130 °C); however, bacterial spores are not reduced in the former. Moreover, pasteurized digestate is prone to recontamination [3].

7.11. Light

Light does not kill methanogens but strongly inhibits methanation. Hence light should be blocked from entering the anaerobic digestion chamber.

7.12. Solid residue/slurry

After the anaerobic degradation is nearly complete, the solid residue or digestate is removed and is normally cured aerobically and screened for items such as glass shards, and plastic pieces before being disposed on land.

The purity of the material fed into the system dictates the quality of the slurry that is produced.

8. Anaerobic digesters/reactors/fermenters

Before proceeding with a brief description of anaerobic digesters/reactors/fermenters, it must be clarified that all the three terms basically mean the same thing and can be used interchangeably. In the anaerobic process the bacteria eat the substrate and digest it, releasing methane, CO₂, etc. The term 'digestion' is based on this fact. The anaerobic process releases gases due to microbial action as happens in fermentation. Hence it is also called 'anaerobic fermentation' or just 'fermentation'. And since what happens is essentially a biological process with associated chemical/biochemical reactions, it can be rightly called a 'reaction'. Hence the vessel in which anaerobic digestion is carried out can be called an 'anaerobic reactor'.

A 'biogas digester' is also an essentially anaerobic digester/fermenter/reactor. This term is used for systems which are employed primarily for biogas production as distinct from other terms which are applied to systems which are primarily used for waste treatment and in which biogas is but a major by-product [16].

It is necessary to stress upon one more aspect. The step in organic matter degradation which leads to methane is purely anaerobic and is controlled by a consortium of methanogenic bacteria. But, as described earlier, there are other steps of organic matter degradation which must occur before the methanogenesis step [103]. Those steps do not involve strict anaerobes but, rather, several species of cellulolytic, acidogenic, and acetogenic bacteria which are aerobic or facultative. In the so-called 'anaerobic' digester/fermenter/reactor all degradation is, therefore, not truly anaerobic. Only the decisive step, of methane generation, is strictly anaerobic.

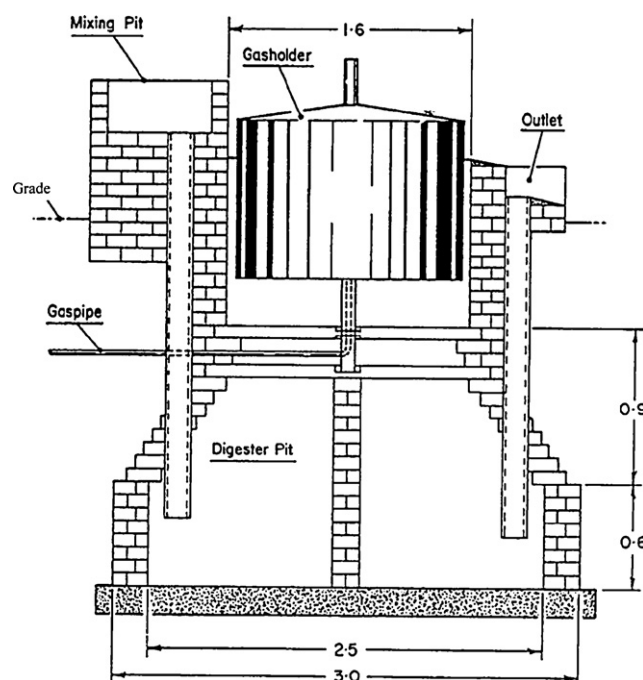


Fig. 4. A floating dome biogas digester.

9. 'Low-rate' and 'high-rate' anaerobic reactors

The biogas digesters used by farmers in India, China and other developing countries basically contain a large chamber of volume, 1000 L (1 m³) or more. In it animal dung mixed with water is fed from one side each day and the overflow of partially digested slurry is collected in a sump at the other side each day. The volume of the daily dung-water slurry feed is about 1/40–1/50 of the reactor volume. The biogas is generated continuously and is temporarily stored in a fixed or a floating dome (Figs. 4 and 5) from where it is drawn for use through a pipe fitted with an on-off control.

In chemical engineering parlance these are 'semi-batch' and 'poorly mixed' reactors [153,154] with a hydraulic retention time (HRT) of 40–50 days. The HRT value is derived from:

$$\text{HRT} = \frac{V_R}{q} \quad (1)$$

where V_R is reactor volume and q is volumetric flow rate of the reactants.

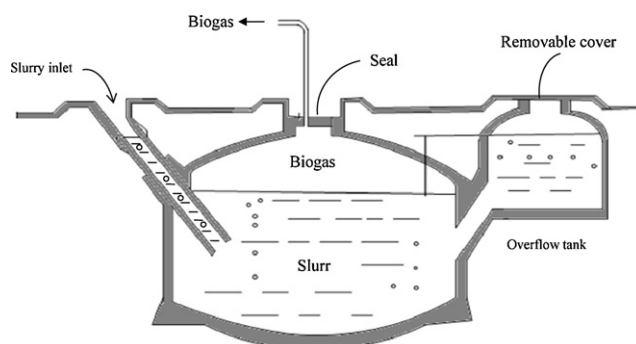


Fig. 5. A typical 'fixed-dome' digester; it is believed that the Chinese were the first to use this concept. As the digestion occurs, biogas is generated which collects under the fixed dome and pushes some of the slurry to the overflow tank. When the gas is taken out for use, its pressure inside the dome is reduced and some of the slurry returns from the overflow tank.

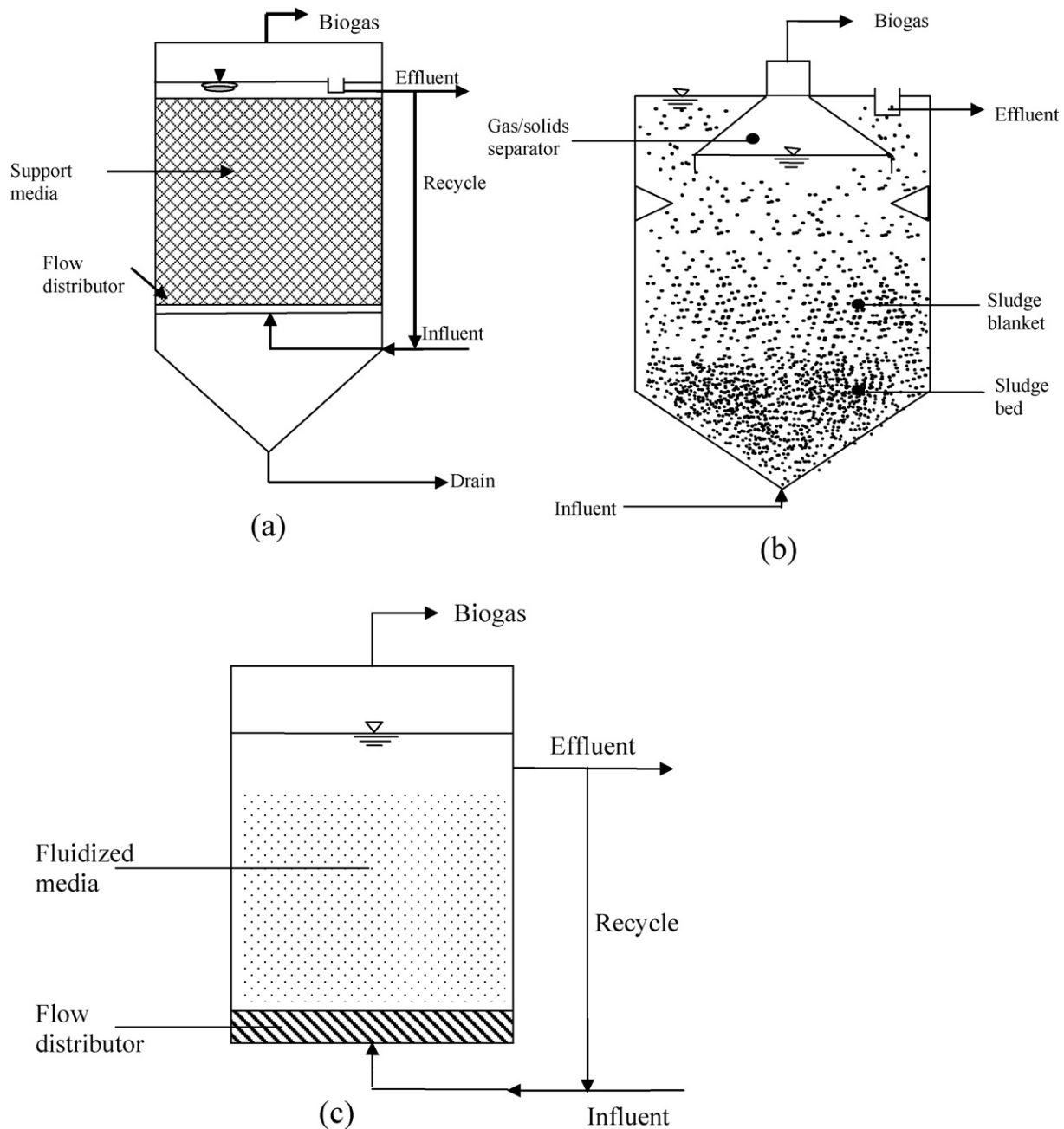


Fig. 6. Examples of 'retained biomass digesters' in which microorganisms are retained for long times even as digester feed keeps passing out; hence $SRT \gg HRT$: (a) anaerobic fixed reactor; (b) UASB; (c) fluidized bed reactor.

For a digester of 2000 L volume, fed at the rate of 40 L of cowdung–water slurry per day (d):

$$HRT = \frac{2000}{40} \frac{L}{(L \text{ d}^{-1})} = 50 \text{ d}$$

If the same digester is fed 50 L of cowdung–water slurry,

$$HRT = \frac{2000}{50} \frac{L}{(L \text{ d}^{-1})} = 40 \text{ d}$$

It has been established [136] that 70–80% of the total cost of most processes is made up of the cost of the concerned reactors; the operational cost is only of the order of 20–30%. Hence if the cost of any process is to be reduced then, other things being equal, the HRT of its reactants must be reduced because lower the HRT, smaller would be the size of the reactor that would be needed.

A very high HRT of 40–50 days is needed in the 'low-rate' digesters mentioned above to accomplish significant extent of anaerobic digestion. But this requirement of HRT is too high compared to the aerobic activated sludge process and other 'high-rate' aerobic processes which have been commonly employed all over the world. In the 1950s the 'anaerobic activated sludge process' was developed as a parallel to the aerobic activated sludge process. It is now referred as a 'first generation high-rate process' [155]. But even that anaerobic activated sludge reactor, which was continuously stirred and also heated to maintain it at temperatures of $\sim 35^\circ\text{C}$ (so that anaerobic digestion could occur at a faster rate) needed HRTs of the order of 10–15 days [155].

This 'slowness' of anaerobic digestion process was the major impediment in the widespread use of the process in spite of the advantage that the process generated a useful by-product in the form of a clean fuel.

Then one after another breakthroughs occurred in anaerobic reactor design beginning with the introduction of anaerobic filter by Young and McCarty [156]. Anaerobic baffled reactor (ABC), UASB (upflow anaerobic sludge blanket) reactor, downflow fixed film reactors, expanded/fluidized bed reactor, diphasic/triphasic reactor, and anaerobic sequencing batch (ASB) reactors were introduced one after another by different scientists within a decade of the introduction of the anaerobic filter [85,157–163]. The common feature of all these reactors is that they utilize one or the other means to retain active mass of anaerobic microorganisms in the reactor even as the waste-to-be-treated is made to travel through the reactor at much faster rate than in the 'low-rate' anaerobic digesters. This enables low HRTs to be maintained while at the same time achieving high SRTs (solid retention times); 'solids' here implying microorganisms. In essence the endeavor has been to:

- **Minimize HRT:** This can be achieved by minimizing V_R and maximizing q as in Eq. (1).
- **Maximize SRT:** This can be accomplished by finding ways and means by which microorganisms are retained much longer in the digester (Fig. 6). This is achieved in 'attached growth systems' by providing anchors to microorganisms in the form of solid support systems as in 'anaerobic filters'. It is achieved in 'suspended growth systems' like 'upflow anaerobic sludge blanket reactors' by developing a highly active sludge of good settling quality and providing other means so that the microorganism – bearing sludge does not get washed out along with exiting treated influent [22].
- **Minimize food-to-microorganism (F/M) ratio:** this is achieved by enhancing SRT/HRT ratio, as above.
- **Enhance the digester loading:** Whereas HRT represents 'volumetric loading', the so called 'digester loading' represents 'mass loading'. This aspect is important because different digester feeds (substrates) may contain different concentrations of digestible organics. Hence at identical HRTs a more concentrated substrate will engage more microorganisms and produce more biogas than a less concentrated substrate. This aspect is brought to the fore in high-solids or 'dry' anaerobic digesters [17,27].

The mass loading rate, normally expressed in $\text{kg m}^{-3} \text{d}^{-1}$ is given by:

$$L = \frac{C_1}{\text{HRT}} \quad (2)$$

where C_1 is the concentration (usually expressed as kg m^{-3}).

Further improvements in the design and operation of high-rate digesters over the years have enabled the anaerobic digestion process to be used for wastewaters of widely different strengths and compositions. The problems associated with process stability and range of applicability have also been solved to a large extent [16,164].

A logical question may be asked at this stage: if high-rate digesters have so many virtues why are low-rate digesters used at all?

The answer is that in their context, for conversion of animal waste energy at a small-scale and in a dispersed manner required in rural and suburban settings, low-rate digesters have a useful role. They are economically viable and are net energy producers even at the small scale at which they are operated. High-rate digesters would not be economically viable at the small scales at which low-rate digesters are successfully utilized. This is because high-rate digesters need much more rigorous, and higher, level of technical supervision than low-rate 'biogas plants'. Hence 'low-rate' digesters will continue to serve a useful purpose even as ever greater advancements occur in high-rate digester technology.

10. Summary

The paper briefly recapitulates the origin and the definition of the terms 'biogas' and 'anaerobic digestion'. It then reviews the impact of biogas on global warming and deals with the implications of methane capture as a means to not only prevent global warming but also generate a fairly clean source of energy. The factors with which extraction of biogas from different types of biodegradable waste can be maximized are then covered.

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